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GRAIN-SIZE-DEPENDENT THERMAL TRANSPORT PROPERTIES IN NANOCRYSTALLINE YTTRIA-STABILIZED ZIRCONIA

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ABSTRACT

Understanding the role of grain boundaries in controlling heat flow is critical to the success of many envisioned applications of nanocrystalline materials. This study focuses on the effect of grain boundaries on thermal transport behavior in nanocrystalline yttria-stabilized zirconia (YSZ) coatings prepared by metal-organic chemical vapor deposition. A strong grain-size-dependent reduction in thermal conductivity is observed at all temperatures from 6–480 K. The behavior is due primarily to the effect of interfacial (Kapitza) resistance on thermal transport. In response to the application of heat to a material, interfacial resistance results in a small temperature discontinuity at every grain boundary, an effect that is magnified in nanocrystalline materials because of the large number of grain boundaries. The observed behavior in YSZ is compared with predictions derived from a diffuse-mismatch model. Implications for the possible development of improved thermal barriers based on nano-layered structures with large interfacial thermal resistance are discussed.

INTRODUCTION

The efficiency of gas turbine engines is dictated by the maximum sustained operating temperature of their typically Ni- or Co-based alloy turbine rotors. Recent studies have concluded that significant near-term progress in increasing turbine engine operating temperatures is more likely to come from the development of improved thermal barrier coatings (TBCs), typically yttria-stabilized zirconia, than from the design of new alloys. New processing techniques that result in TBC microstructures with lower thermal conductivity could lead either to higher operating temperatures of turbine engines, resulting in greater efficiency, or thinner coatings for the same operating temperature, which would reduce overall weight. Using nanocrystalline YSZ coatings offers the possibility of lowering thermal conductivity, and may also provide additional benefits for TBC applications because of the possibility of improved toughness and ductility compared to that of coarser-grained ceramics.

Recent studies of thermal conductivity in nanocrystalline YSZ coatings have shown a very strong grain size dependence for average grain sizes below approximately 40 nm [1]. Studies of the grain size and temperature dependence of the thermal conductivity in YSZ have been interpreted in terms of the interfacial (Kapitza) resistance to thermal transport [2]. This report summarizes the results of those studies and extends them to include a comparison of the experimental observations with predictions of a diffuse mismatch model.

EXPERIMENTAL PROCEDURES

Nanocrystalline YSZ coatings with thicknesses of 500-to-1200 nm were grown on polished polycrystalline α-Al_2O_3 substrates by metal-organic chemical vapor deposition [1]. Samples with controlled average grain sizes from 10-100 nm were produced by varying the processing conditions, primarily the substrate temperature. Yttria contents for all samples used in this study varied from 8-15 mol.%, resulting in formation of the expected cubic fluorite-type structure [3]. Samples were found to contain approximately 10% porosity based on nanoindentation [1] and small-angle neutron scattering studies [4], independent of grain size. No dependence of thermal conductivity on Y_2O_3-content was observed, providing additional confidence that the observed behavior was due to intrinsic grain-size effects.

Thermal conductivity was measured using the 3ω method [5,6]. A typically 25 μm-wide and 300 nm-thick Au/Cr line was patterned onto the sample surface by electron beam evaporation and photolithography for use as both sample heater and thermometer in these measurements. Samples were placed in a liquid-helium cryostat in a low pressure gaseous helium environment for thermal conductivity measurements at temperatures from 6-280 K. Measurements from 280-480 K were performed in vacuum using a high-temperature probe station [7]. The data were corrected to account for the approximately 10% porosity in the samples.

RESULTS AND DISCUSSION

Recent studies of thermal conductivity in nanocrystalline YSZ coatings have shown a very strong grain size dependence for average grain sizes below approximately 40 nm [1]. As seen in Fig. 1, at room temperature the thermal conductivity of YSZ with 10 nm grain size is reduced more than a factor-of-two compared to that of coarse-grained coatings. In the case of YSZ, this reduction is primarily due to the increasing contribution with decreasing grain size of the interfacial (Kapitza) resistance to thermal transport, which, as shown in Fig. 2, results in a temperature discontinuity at every interface in response to an applied heat flux. The temperature difference across a single grain can be described, therefore, as the sum of the temperature difference across a single grain interior region and the average temperature discontinuity at a grain boundary. The measurable thermal conductivity of a polycrystalline material, k, can be defined [2, 8] as:

$$k = \frac{k_o}{1 + \frac{k_o R_k}{d}} , \qquad (1)$$

where k_o is the grain interior thermal conductivity, d is the grain size, and R_k is the Kapitza resistance [2, 8]. The parameters k_o and R_k can be determined by fitting plots of k vs. d to Eq. 1. A typical fit is shown in Fig. 1. The obtained values of the Kapitza conductance, $G = 1/R_k$, are shown as closed circles in Fig. 3. The conductance increases as temperature increases and plateaus in the vicinity of 300 K.

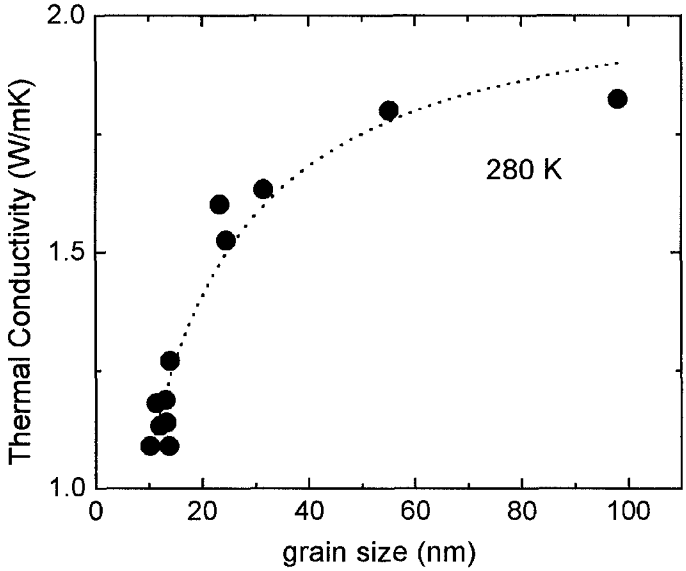

Figure 1. Thermal conductivity versus grain size at 280 K. Line represents a fit to Eq. 1.

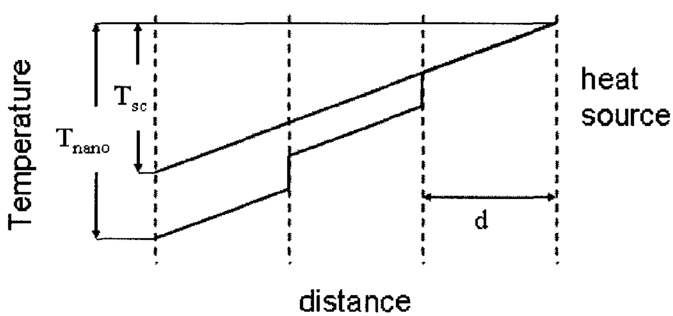

Figure 2. Schematic representation of the one-dimensional temperature profile across single crystal and polycrystalline material in response to an applied heat flux. The temperature drop across a nanocrystalline material, T_{nano}, is larger than that across a single crystal, T_{sc} due to the many temperature discontinuities at grain boundaries. This results in a reduction of the net thermal conductivity, which becomes increasingly significant as grain size is reduced.

The Kapitza conductance is the derivative of the net heat flux transmitted across an interface with respect to the temperature difference across the interface. In the diffuse mismatch model, it is assumed that all phonons are scattered diffusely at an interface and the correlation between the incoming and outgoing phonons is completely destroyed by the scattering [9]. The transmission probability is determined by a mismatch between phonon densities of states. The Kapitza conductance can be expressed as

$$G = \frac{1}{4}\sum_j v_{1,j} \int_0^\infty \alpha_1 \hbar\omega \frac{d}{dT}\{D_j(\omega)n(\omega,T)\}d\omega \ , \tag{2}$$

where $v_{1,j}$ and $D_j(\omega)$ are the velocity and the density of states for phonons with mode j on the incident side of the interface, respectively, α_1 is the transmission probability across the interface, and $n(\omega)$ is the occupation number of a phonon with energy $\hbar\omega$ [5]. Assuming that both sides of an interface have an identical structure (α_1 assumed to equal 0.5 in this case), Eq. 2 is calculated for polycrystalline YSZ using the Debye model. The results of the calculation are denoted as open circles in Fig. 3. At all temperatures, the

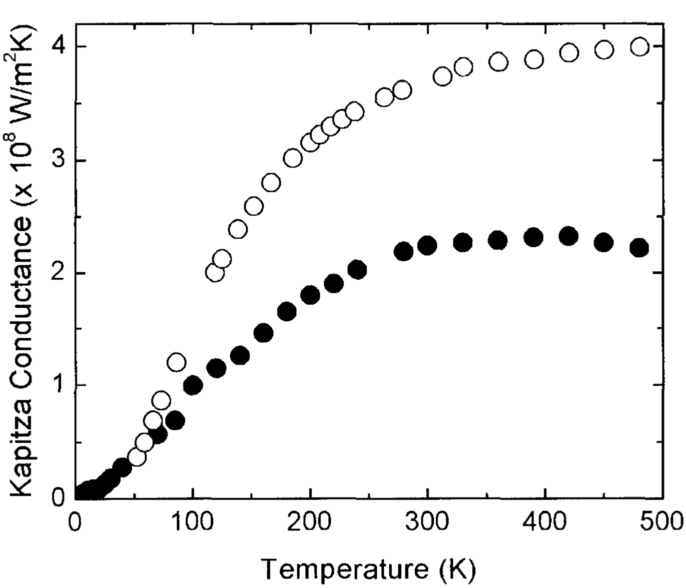

Figure 3. Kapitza conductance, G, for YSZ derived from the measured grain-size dependent thermal conductivity (●) and predicted with the diffuse mismatch model (○).

calculation of G with the diffuse mismatch model predicts higher Kapitza conductance values than those obtained from fits of the measured k vs. grain size to Eq. 1. The structures on both sides of a grain boundary would be different due to the random orientation of grains in polycrystalline materials. This needs to be considered in determining the transmission coefficient. However, simply using a value for α_i other than 0.5 does not improve the agreement with the G values calculated using Eq. 1. The deviation of the calculated G becomes larger with increasing temperature because the Debye model breaks down at high temperatures. For this reason, we believe that the G values calculated from Eq. 1 are more accurate than those determined from a diffuse mismatch approach.

While YSZ is the material of choice in most current TBC applications, our studies suggest that an effective new strategy in designing TBC's with lower thermal conductivity could be to search for materials with large Kapitza resistance. Little is currently known about the magnitude of the average Kapitza resistance in different materials. At nanocrystalline grain sizes, materials with bulk thermal conductivity larger than that of YSZ could actually have a smaller net thermal conductivity. Nanocomposites of two or more dissimilar materials could be prime candidates for future TBC applications, both because the interfaces in such systems could exhibit large Kapitza resistance, and because formation of composite microstructures is a strategy that has been demonstrated to be effective in stabilizing nanocrystalline grain sizes to the high temperatures that would be encountered.

CONCLUSIONS

The observed grain size dependent reduction in thermal conductivity of nanocrystalline YSZ is believed to arise primarily due to the Kapitza resistance to thermal transport at grain boundaries. The temperature-dependent Kapitza resistance in polycrystalline materials can be determined from measurements of grain-size dependent thermal conductivity and compared with the predicted values obtained from a diffuse mismatch model. Even in a highly defective material like YSZ, a substantial reduction in thermal conductivity is obtained by increasing the number-density of grain boundaries through grain refinement to the nanometer scale. Comparisons of the magnitude of the average Kapitza resistance in YSZ with that in other material are desirable. It is possible that future studies of other materials could lead to the development of improved thermal barriers by identifying materials possessing both low bulk thermal conductivity and large Kapitza resistance.

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